

CHEMOSELECTIVE OXIDATION OF 6,13-BIS(DECYLTHIO)PENTACENE

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**Chemoselective oxidation of 6,13-Bis(decylthio)pentacene**

by

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## ABSTRACT

Organic semiconductors present much potential for industrial use because of their possible low cost production. Pentacene and pentacene derivatives are promising candidates for organic semiconductor research since their  $\pi$ -conjugated electronic structures possess small HOMO-LUMO gaps and high field effect mobility. Whereas there is much potential in devices made from pentacenes they do however undergo short lifetimes and poor processability due to photodegradation and poor solubility of pentacene. Previous research has shown that the pentacene lifetime and solubility can be enhanced by arylthio and alkylthio substituents placed on the pentacene backbone. For example 6,13-*Bis*(decylthio)pentacene was one of the longest lived pentacene derivative known and it has been shown to exhibit excellent solubility in a variety of organic solvents. This research was performed to chemically control the chemoselective oxidation of the compound 6,13-*Bis*(decylthio)pentacene to produce a new pentacene derivative bearing either sulfoxide or sulfone functional groups thus forming a new pentacene derivative which may show greater photooxidative resistance. The products of this experiment were as follows: 6-(decylsulfinyl)-13-decylthio)pentacene and 6,13-*Bis*(decylsulfinyl)pentacene as characterized by NMR, UV, mass spectra, and electrochemical techniques. The half-life of 6-(decylsulfinyl)-13-decylthio)pentacene was longer (2900 min) compared to the starting material and 6,13-*Bis*(decylsulfinyl)pentacene. However, both products had similar HOMO-LUMO gaps as determined by cyclic voltammetry. Using 0.5 equivalent of *m*CPBA gave the maximum yield (76%) of 6-(decylsulfinyl)-13-decylthio)pentacene. This product was a better semiconductor due to higher stability.



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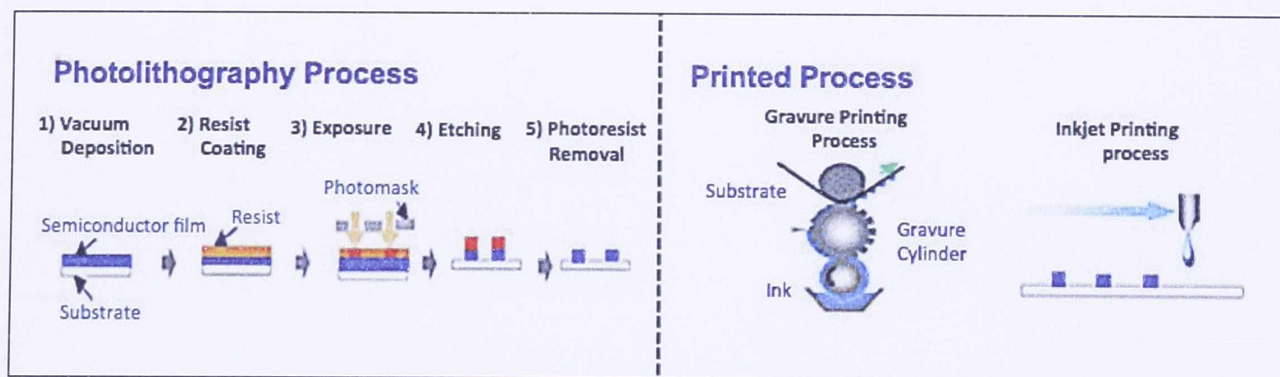
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## CHAPTER 1: INTRODUCTION

### 1.1 Organic Semiconductor

Organic semiconductors are carbon-based materials in microelectronics that have semiconducting properties<sup>1-2</sup>. Lately, organic semiconductors have been applied widely as active elements in various optoelectronic devices such as organic light emitting diodes, organic photovoltaics, and organic field effect transistors<sup>3-8</sup>. The organic semiconducting materials offer benefits such as lower production costs and are also easier to manufacture, due to flexible and lightweight properties (Figure 1)<sup>9-15</sup>. Also, the remarkable properties of these organic semiconductor materials make it possible to fabricate them using less toxic and environment-friendly hydrogen-carbon based materials. Organic semiconducting materials have the potential to produce advanced new functionalities such as biological and chemical sensing that would otherwise be impossible to produce using inorganic electronics such as silicon devices<sup>16-29</sup>.

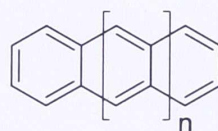


**Figure 1.** Fabrication process comparison of silicon semiconductors (photolithography process) and organic semiconductors (printed process)



## 1.2 Introducing Acenes for Organic Semiconductors

Acenes are polycyclic aromatic hydrocarbons, or linear arrays of fused benzene rings numbering three or more. These are an exciting class of small organic molecules showing great promise in the development of organic semiconductors. These acenes, in general, are fully conjugated molecules; every  $\pi$ -bond is conjugated with at least two others. This association of  $\pi$ -bonds



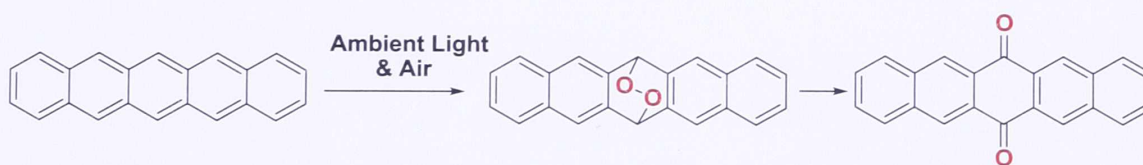
**Figure 2.** General structure of acenes

allows the  $\pi$ -electrons to move throughout the molecule. In addition to this, the ability to move  $\pi$ -electrons throughout the molecule accounts for semiconducting properties<sup>30</sup>. This can best be described by the difference in energy gaps between the highest energy occupied molecular orbital (HOMO), and the lowest energy unoccupied molecular orbital (LUMO) in the molecules. As the gap becomes smaller, it is easier for electrons to switch between the HOMO and LUMO<sup>31-37</sup>. When the molecules are close enough that their  $\pi$ -systems overlap, the electron from HOMO of one molecule can jump to the LUMO of another. This mechanism allows electrons to flow through the material allowing electrical signals to be transmitted, and these properties make the material a good semiconductor.

### 1.3 Pentacene

#### 1.3.1 Advantage and Drawbacks of Pentacene

Due to the comparative ease of synthesis, odd numbered compounds are the most studied; pentacene has received much attention due to its promise as an active semiconducting material and has many applications of organic electronics<sup>38-40</sup>. Interestingly, the parent pentacene is a benchmark in the field of thin film organic electronic devices since its  $\pi$ -conjugated electronic structure, a small HOMO-LUMO gap of 2.2 eV, and strong two-dimensional electronic interactions in the solid state giving rise to  $\pi$ - $\pi$  stacking which facilitates charge transport leading to high mobilities<sup>41-46</sup>. While pentacene is a fairly good semiconductor there are numerous problems that have held back this promising molecule.



**Figure 3.** Photooxidation studies on unsubstituted pentacenes

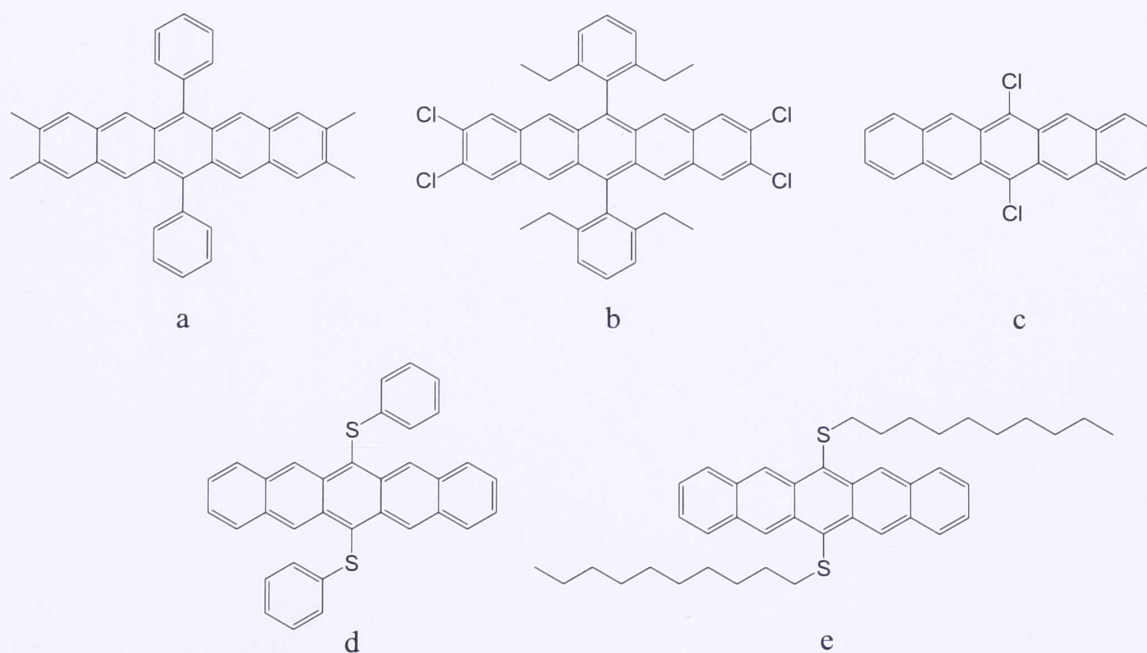
The most significant problems are the lack of solubility, which inhibits solutions-based processing, and the lack of stability, which leads to devices of limited lifetime due to the photodegradation, photooxidation and photodimerization<sup>47</sup>. For example, when pentacene is oxidized, the hydrogen atoms on the central aromatic ring of the molecule are substituted with oxygen at the 6 and 13 carbon sites via double bonds. This resulting pentacene product is known as the 6,13-pentacene quinone. Through this reaction, the conjugated system is broken at the central ring; therefore the oxidizing pentacene reduces the extent of the conjugated  $\pi$ -system



from five rings to four rings<sup>47</sup>. Consequently, this results in an increase in the highest occupied molecular orbital energy, therefore the HOMO-LUMO gap increases and its mobility decreases<sup>48</sup> which prevents immediate device implementation of this semiconducting material. While bare pentacene degrades quickly, the process of photooxidation can be slowed down remarkably by attaching substituents along the pentacene backbone<sup>49</sup>.

### 1.3.2 Pentacene derivatives

Locations of substituents, steric resistance and electronic effect have been reported to affect the stability of pentacene derivatives<sup>50</sup>. A combination of experimental and computational studies of a series of substituted pentacenes including halogenated, phenylated and thiolated derivatives have been analyzed<sup>50</sup>.

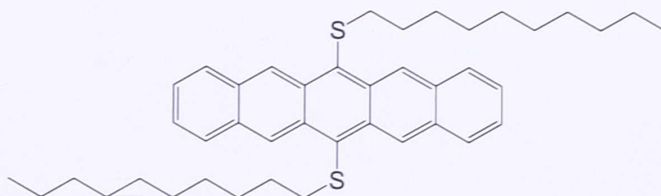


**Figure 4.** Structure of pentacene derivatives with halogenated, phenylated and thiolated derivatives: (a) 2,3,9,10-tetramethoxy-6,13-diphenylpentacene, (b) 2,3,9,10-tetrachloro-6,13-Bis(2',6'-dimethylphenyl)Pentacene, (c) 6,13-dichloropentacene, (d) 6,13-Bis(phenylthio)pentacene, (e) 6,13- Bis(decylthio)pentacene

The combination of results provide for a quantitative assessment of band gaps and photooxidative resistances for a large series of pentacene derivatives as a function of substituents. The most impressive effects on pentacene's stability may be observed with organothio substituents. Electrochemical data indicates strong electronic effects for organothio substituents as these are among the most difficult derivatives to oxidize but also have relatively low HOMO-LUMO energies. The presence of sulfur in the substituent improves the photooxidative resistance of the pentacene derivative by pulling electron density away from the pentacene  $\pi$ -system thereby lowering HOMO-LUMO energies. Also, sulfur atoms of organothio substituents physically quench  $O_2$  and thereby protect the pentacene backbone from oxidation<sup>50</sup>.

#### 1.4 Objectives of the Study

One of the longest lived pentacene derivatives with organothio substituents is 6,13-*Bis*(decylthio)pentacene. This compound has excellent solubility in a variety of organic solvents including methylene chloride, toluene and hexanes.



**Figure 5.** Structure of 6,13-*Bis*(decylthio)pentacene

Given the enhanced photooxidative resistance of the pentacene skeleton in 6,13-*Bis*(decylthio)pentacene, the objective of the study was to seek a method to produce a new pentacene derivative with sulfoxide or sulfone functional groups on 6,13-*Bis*(decylthio)pentacene. If formed, such a derivative may show even greater photooxidative

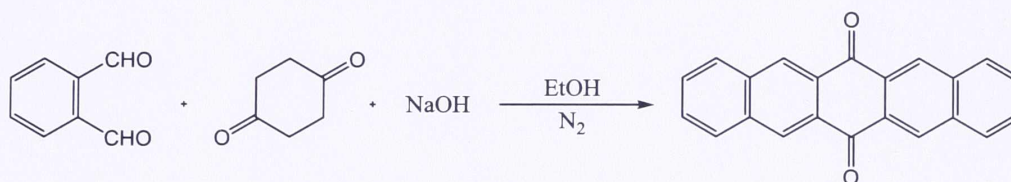


resistance given the electron withdrawing nature of the sulfoxide or sulfone functional groups. Also, the electron withdrawing groups directly attached to the pentacene skeleton should lower both HOMO and LUMO energies, thereby slowing the Diels-Alder cycloaddition of singlet oxygen as well as direct addition of triplet oxygen via an electron transfer pathway.

## CHAPTER 2: EXPERIMENTAL

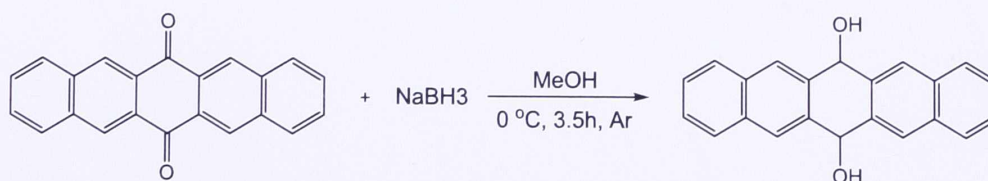
### 2.1 Preparation of 6,13-Bis(decylthio)pentacene

#### 2.1.1 Preparation of 6,13-pentacenequinone



Formation of pentacene dione was achieved by dissolving o-phthalaldehyde (7.0 g, 52.19 mmol) in EtOH(400 mL). After heating to 45 °C for an hour all solids had dissolved and cyclohexane 1,4-dione (2.93 g, 26.16 mmol) was added to the solution and stirred for 15 min. When dissolved completely, 5% NaOH solution (10 mL) was added slowly drop by drop until color of reaction mixture changes from light yellow to dark brown, and finally yellow precipitates were formed. The solution was stirred overnight. Water (100 mL) was added to the reaction, and the resulting yellow precipitate was filtered and washed multiple times with H<sub>2</sub>O. The solid was air dried to yield pure 6,13-pentacenequinone (6.68 g, 83%). The purity of this compound was verified by the spectral data of this compound are given in the appendix (Table 1).

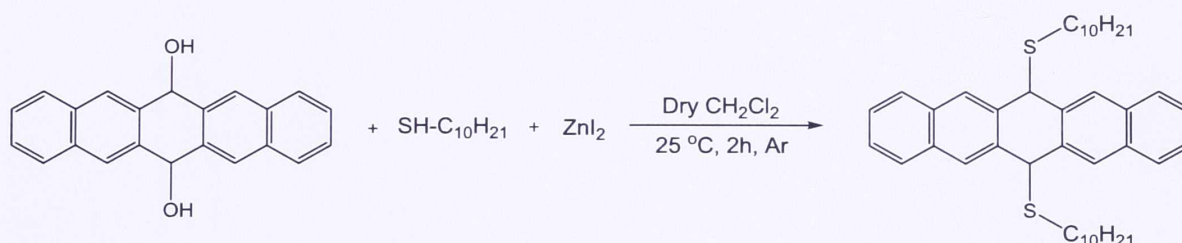
#### 2.1.2 Preparation of 6,13-dihydroxy-6,13-dihyropentacene





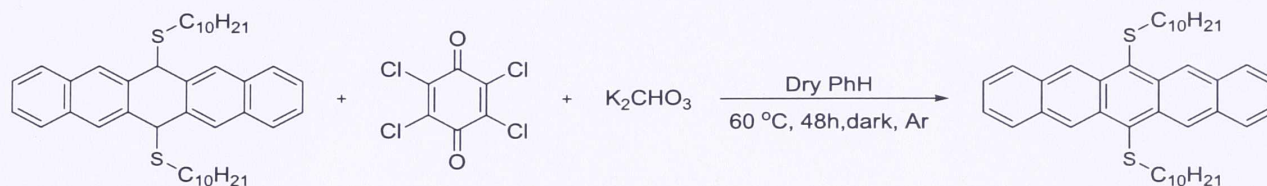
NaBH<sub>4</sub> (1.22 g, 32.46 mmol) was added to a suspension of 6,13-pentacenequinone (1.0 g, 3.24 mmol) in dry MeOH (40 mL) at 0°C under an argon atmosphere. The reaction mixture was stirred at 0°C for 0.5 h and at room temperature for 1 h, and then quenched with H<sub>2</sub>O at 0°C. The resulting mixture was filtered and washed with H<sub>2</sub>O. The resulting solid was taken up in CHCl<sub>3</sub>, then filtered and washed with CHCl<sub>3</sub>, and dried in *vacuo* to give an off-white solid product (0.92 g, 91%) with melting point of 235 °C. The spectral data of 6,13-dihydroxy-6,13-dihydropentacene are given in the appendix (Table 2).

### 2.1.3 Preparation of *cis*-6,13-Bis(*n*-decylthio)-6,13-dihydropentacene



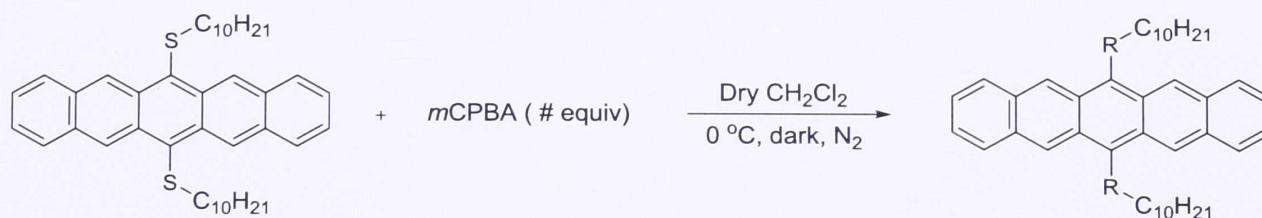
To a mixture of 6,13-dihydroxy-6,13-dihydropentacene (1.0 g, 3.20 mmol) and zinc iodide (1.02 g, 3.20 mmol), dry CH<sub>2</sub>Cl<sub>2</sub> (100 mL) and 1-decanethiol (1.22 g, 7.03 mmol) were added slowly at room temperature under an argon atmosphere. The resulting mixture was stirred for 2 h, and then quenched with H<sub>2</sub>O. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was washed with brine and dried over anhydrous CaCl<sub>2</sub>. After evaporation of solvents, the residue was purified by column chromatography on silica gel eluted with *n*-hexanes-CH<sub>2</sub>Cl<sub>2</sub> (2:1) to give colorless viscous oil as the product (1.80 g, 90% yield). The spectral data of *cis*-6,13-Bis(*n*-decylthio)-6,13-dihydropentacene are given in the appendix (Table 3).

### 2.1.4 Preparation of 6,13-Bis(*n*-decylthio)pentacene



A mixture of *cis*-6,13-Bis(*n*-decylthio)-6,13-dihydropentacene (1.10 g, 1.76 mmol), tetrachloro-1,4-benzoquinone (0.87 g, 3.52 mmol), and  $K_2CO_3$  (2.43 g, 17.6 mmol) in dry benzene (170 mL) was stirred at 60°C for 48 h under an argon atmosphere in the dark. After cooling to room temperature, the reaction mixture was filtered and washed with  $CH_2Cl_2$ . After evaporation of the filtrate, the solid residue was triturated with *n*-hexanes, filtered, and washed with hexane. The solid residue was passed through a short column of *n*- $Al_2O_3$  eluted with  $CH_2Cl_2$  and the deep blue band was collected. The solvent was evaporated to give pure acene as a deep blue solid (0.81 g, 74% yield). The spectral data of 6,13-Bis(*n*-decylthio)pentacene are given in the appendix (Table 4).

### 2.2 Chemoselective oxidation of 6,13-Bis(decylthio)pentacene using *m*CPBA



(#equiv: 0.5, 1, 2, 3, 4 ; R: S=O, S)



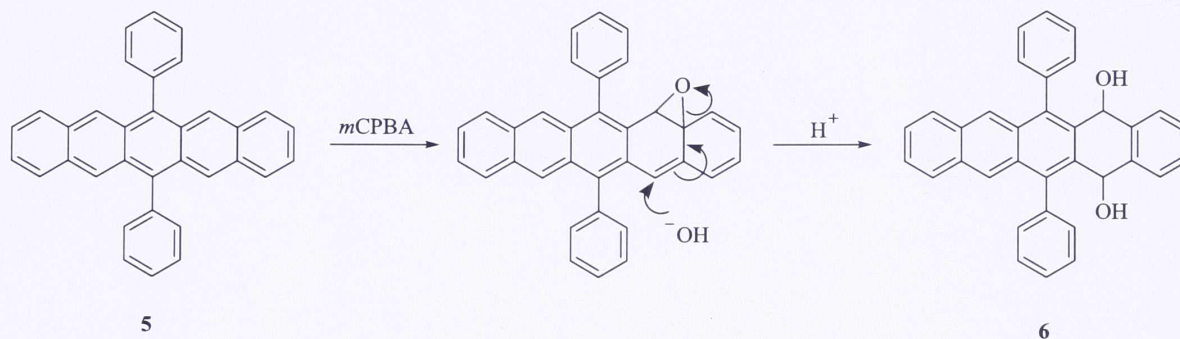
### 2.2.1 6-Decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )

To a solution of 6,13-*Bis*(decylthio)pentacene (10 mg, 0.0016 mmol) in dry DCM (7 mL) at 0°C was added *m*CPBA (# equiv) and reaction mixture was stirred for variable time between 5 and 8 min under a N<sub>2</sub> atmosphere in the dark. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched by addition of saturated solution of NaHCO<sub>3</sub> (10 mL). The reaction mixture was washed with saturated solution of NaHCO<sub>3</sub> (3x10 mL), water (10 mL), and dried over anhydrous CaCl<sub>2</sub>. The organic solvent was evaporated to give crude 6,13-*Bis*(decylsulfinyl)pentacene or 6-decylsulfinyl-13-decylthiopentacene. This was further purified by prep plate chromatography using ethyl acetate and DCM ratio of 1:9 to get a yield of 72 % (3.7 mg) of product (**2** in Scheme 1). The spectral data are given in the appendix (Table 6).

### 2.2.2 6,13-*Bis*(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )

To a solution of 6,13-*Bis*(decylthio)pentacene (5.0 mg, 0.008 mmol) in dry DCM (7 mL) at 0 °C was added *m*CPBA (4.1 mg, 0.023 mmol) and reaction mixture was stirred for 7 min under a N<sub>2</sub> atmosphere in the dark. The progress of the reaction was monitored by TLC. Upon completion, the reaction was quenched by addition of saturated solution of NaHCO<sub>3</sub> (10 mL). The reaction mixture was washed with saturated solution of NaHCO<sub>3</sub> (3x10 mL), water (10 mL), and dried over anhydrous CaCl<sub>2</sub>. Evaporation of the organic solvent followed by washing of crude solids with methanol gave pure product ( $\pm 3$  and  $\pm 4$ ) in 65% yield (3.4 mg). The spectral data are given in the appendix (Table 7).

### 2.3 Oxidation of 6,13-diphenylpentacene using *m*CPBA to form 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol



To a solution of 6,13-diphenylpentacene (10 mg, 0.023 mmol; **5** in Scheme 2) in dry DCM (15 mL) at 0°C was added *m*CPBA (9 mg, 0.041 mmol) and reaction mixture was stirred for 45 min at room temperature under a  $\text{N}_2$  atmosphere in the dark. The reaction gave a crude product which was further purified by prep plate chromatography using DCM to yield a pure product (**6** in Scheme 2) with 20% yield (0.002 g). The spectral data are given in the appendix (Table 8).

## 2.4 Equipment

### 2.4.1 NMR and Mass Spectrometry

$^1\text{H}$  NMR (500 MHz) spectra were recorded with a Varian AC 500 spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR samples were internally referenced to TMS (0.00 ppm). Mass spectra were determined on LDI-TOF-MS (Shimadzu-Biotech) mass spectrometer. High-resolution mass spectra were recorded at the Notre Dame mass spectrometry facility.



### 2.4.2 UV-Vis Spectroscopy and Kinetic Studies

UV-visible spectra were obtained on a Nikolet Evolution 300 spectrometer using 1 cm quartz cells. Dilute solutions ( $2.0 \times 10^{-4}$  M) of pentacene derivatives were prepared using degassed spectroscopic grade dichloromethane. The cells were protected from light until each experiment began, at which point an initial spectrum was recorded. Each cell was then exposed to air by loosening the cap to allow for free exchange of air, while minimizing solvent evaporation. The cells were placed on a laboratory bench under conventional 32 W, SP35 fluorescent lighting (General Electric, 2850 lm). The solutions were repeatedly scanned at prescribed intervals until less than 5% of the starting acene remained.

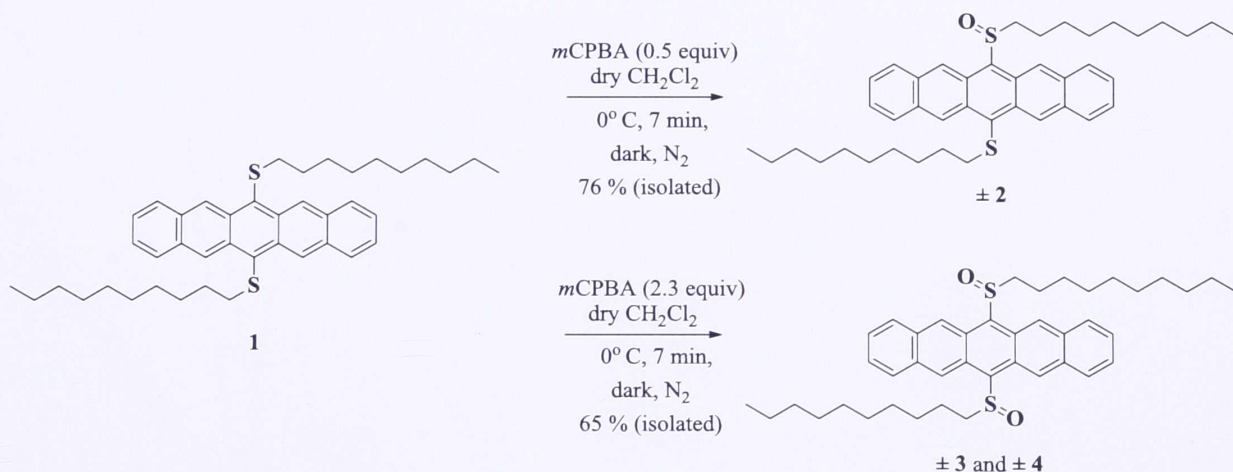
### 2.4.3 Cyclic Voltammetry

Cyclic voltammetry (CV) studies of each pentacene derivative were performed using a BAS-100B electrochemical analyzer in a three-electrode single-compartment cell with a Pt working electrode, Ag/AgCl reference electrode, and a Pt wire as auxiliary electrode. Tetrabutylammonium hexafluorophosphate, TBAPF<sub>6</sub>, was used as supporting electrolyte (0.1 M), and HPLC grade dichloromethane was used as solvent (no further purification). A scan rate of 100 mV/s was typically employed. The concentration of pentacene derivative was typically 0.5 mM. The Pt working electrode required cleaning between samples, especially before and after characterization of S containing **1** and **2**. HOMO and LUMO energies and electrochemical HOMO-LUMO gaps were determined from the onsets of the first oxidation and the first reduction waves.

## CHAPTER 3: RESULTS AND DISCUSSION

### 3.1 Synthesis of monosulfoxide ( $\pm$ 2) and bissulfoxides ( $\pm$ 3, and $\pm$ 4)

In order to explore the oxidation behavior, 6,13-*Bis*(decylthio)pentacene was treated with 0.5 to 4 equivalents of *meta*-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane at 0 °C for variable times between five and eight minutes. The reactions were quenched with saturated sodium bicarbonate solution. Crude products were isolated via dichloromethane extraction, dried, evaporated and characterized. Relatively simple reaction conditions were found to synthesize monosulfoxide ( $\pm$  2) and bissulfoxides ( $\pm$  3, and  $\pm$  4) in good yield (Scheme 1). Thus, reacting **1** with 0.5 eq. of *m*CPBA for seven minutes at 0 °C produced  $\pm$  2 as the major product in roughly 76 % isolated yield. Treating **1**, with 2.3 eq. of *m*CPBA for seven minutes at 0 °C produced a mixture of bissulfoxide diastereomers,  $\pm$  3 and  $\pm$  4, in roughly 65 % yield.



**Scheme 1.** Synthesis of monosulfoxide ( $\pm$  2) and bissulfoxides ( $\pm$  3 and  $\pm$  4) of 6,13-*Bis*(decylthio)pentacene (**1**)



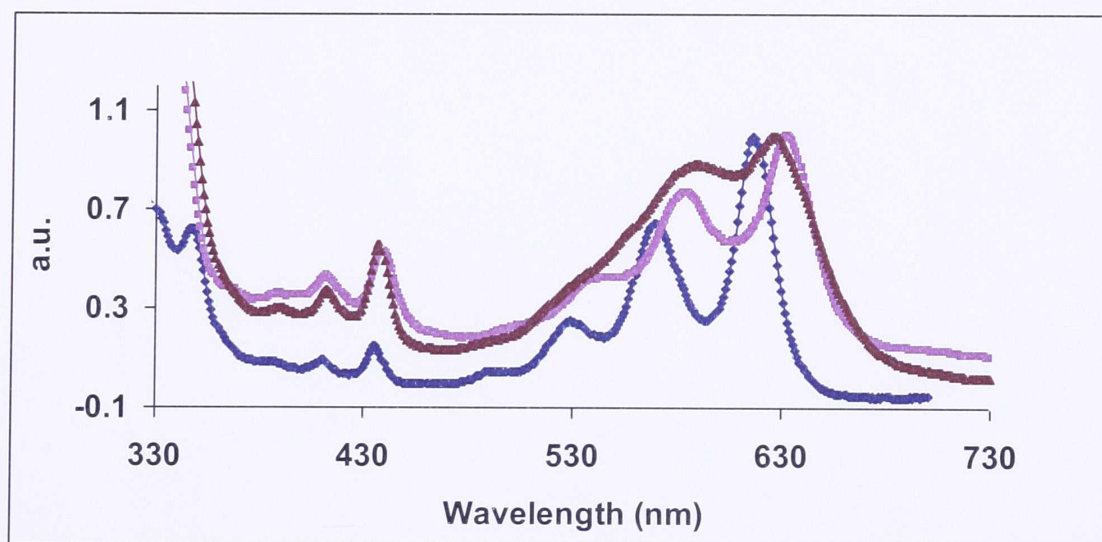
Utilizing larger quantities of *m*CPBA gave reaction mixtures that might have included sulfone derivatives, but these mixtures were not pure. Moreover, attempted separation of these mixtures via preparative silica thin layer chromatography led to rapid degradation of the suspected sulfone derivatives.

### 3.2 Characterizations of new pentacene derivatives by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy

The single sulfoxide group in  $\pm \mathbf{2}$  was evident by careful examination of the  $^1\text{H}$  NMR spectrum (Figures 8 and 9) that included a pair of multiplets at approximately 3.3-3.4 (1H) and 3.8-3.9 ppm (1H) corresponding to the diastereotopic methylene protons adjacent to the sulfoxide group. By contrast, the methylene protons of  $\pm \mathbf{2}$  that were adjacent to the sulfide sulfur resonated at approximately 3.0-3.1 ppm (2H) and appeared as a clean triplet. Likewise the  $^{13}\text{C}$  NMR spectrum (Figure 10) of  $\pm \mathbf{2}$  revealed two signals for the same two methylene carbons, one at approximately 39 ppm (C-S) and one at approximately 54 ppm (C-SO). Evidence existed for the slow rotation of the decylsulfinyl group in  $\pm \mathbf{2}$  with respect to the pentacene backbone. Thus, the  $^1\text{H}$  NMR spectrum showed a relatively sharp singlet at approximately 9.8 ppm due to the "X" protons (2H) of the pentacene backbone at C12 and C14. These corresponded to the aromatic protons that were closest to the sulfide function. However, the "X" protons of the pentacene backbone at C5 and C7 (i.e. the aromatic protons closest to the sulfoxide function) were observed as a pair of severely broadened signals (1H each) at approximately 9.3 and 10.4 ppm. While these protons were diastereotopic, they were too far removed from the sulfoxide group to be split into a pair of signals in the absence of a slow rotation phenomenon. Likewise, their broadened nature was consistent with a dynamic rather than a configurational explanation. The  $^1\text{H}$  NMR spectrum (Figures 12-14) of the mixture  $\pm \mathbf{3}$  and  $\pm \mathbf{4}$  also revealed broadened signals,

consistent with slow rotation of both decylsulfinyl groups about the pentacene backbone. Two signals corresponding to the diastereotopic methylene protons were observed at approximately 3.3 and 3.8 ppm (2H each). Severely broadened proton signals corresponding to the “X” protons of the pentacene backbone (i.e. those attached to the 5, 7, 12 and 14 carbons) were observed at approximately 9.3 and 10.5 ppm (2H each). It was remarkable that pentacene derivative **1** chemoselectively oxidized at S rather than the normally highly reactive<sup>47</sup> acene pi system. This result suggested that the sulfur atoms of **1** effectively shielded the acene pi system from reactive oxygen species including *m*CPBA and perhaps airborne oxygen as well.

### 3.3 UV-Vis and Cyclic Voltamogram of mono and bissulfoxide pentacene

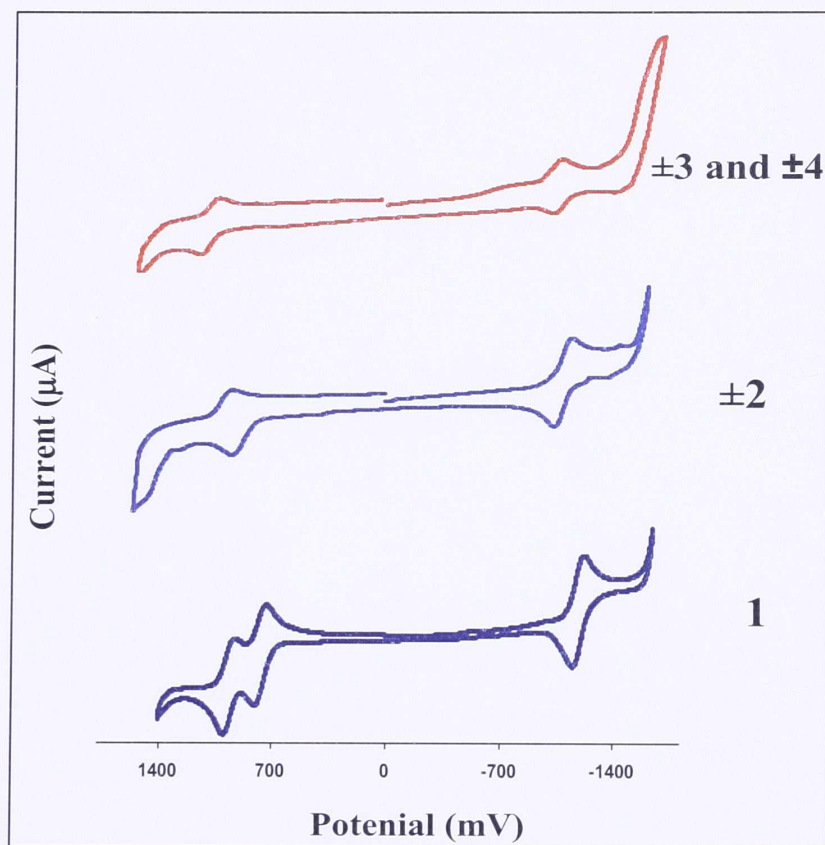


**Figure 6.** UV-Vis Spectra for **1** (blue line), **± 2** (red line), and the mixture of **± 3** & **± 4** (pink line)

Figure 6 shows a comparison between the UV-vis spectra for **1**, **± 2** and the mixture of **± 3** & **± 4** revealing red-shifted absorptions for the longest wavelength bands upon sulfoxide formation. A 17 nm shift was observed in the longest wavelength band for 6,13-*Bis*(decylsulfinyl)pentacene (**±**



**3** &  $\pm$  **4**;  $\lambda_{\text{max}}$  634 nm) compared to **1** ( $\lambda_{\text{max}}$  617 nm) indicating to a modest reduction in the corresponding HOMO-LUMO gap by approximately 0.04 eV. Cyclic voltammograms for these compounds illustrated in Figure 7, suggested a similarly small HOMO-LUMO gap reduction upon moving from **1** to  $\pm$  **3** &  $\pm$  **4** (0.07 eV). The data is summarized in Table 1.



**Figure 7.** Cyclic voltammograms for **1**,  $\pm$  **2**, and the mixture of  $\pm$  **3** &  $\pm$  **4**

The cyclic voltammograms allowed for direct measurement of HOMO and LUMO energies revealing, as expected, a reduction in their values upon formation of sulfoxide functions (Table 1). Thus, the HOMO and LUMO energies for  $\pm$  **2** were 0.08 and 0.13 eV smaller than those of **1**. Likewise, the HOMO and LUMO energies for the mixture of  $\pm$  **3** and  $\pm$  **4** were 0.26 and 0.33 eV

smaller than those of **1**. These numbers suggested a possible enhancement in photooxidative resistances upon sulfoxide formation.

**Table 1.** Photooxidative, optical and electrochemical properties of pentacene derivatives **1**,  $\pm 2$ , and the mixture of  $\pm 3$  and  $\pm 4$ .

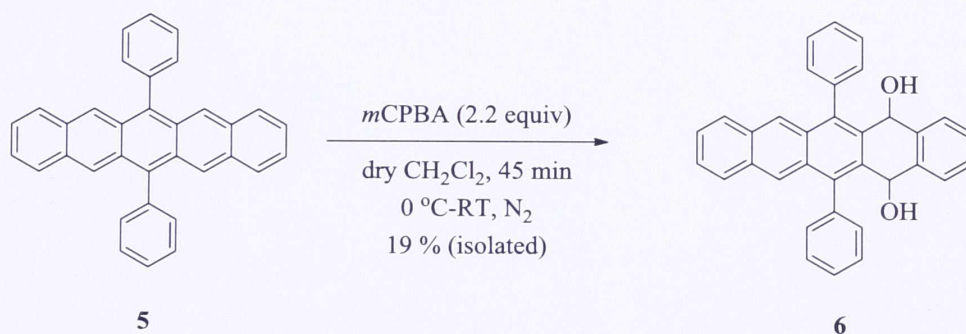
	Half life (min)	Low energy $\lambda_{\text{max}}$ (nm)	$E_{\text{g, opt}}$ (eV)	$E_{1/2}$ [O] (mV)	$E_{1/2}$ [red] (mV)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$E_{\text{g, EChem}}$ (eV)
<b>1</b>	750	617, 570, 529	<b>1.88</b>	755 936	-1229 -1726	-5.07	-3.26	<b>1.81</b>
$\pm 2$	2900	627, 590, 536	<b>1.85</b>	875	-994	-5.15	-3.39	<b>1.76</b>
$\pm 3$ & $\pm 4$	200	634, 584, 544	<b>1.84</b>	1012	-885	-5.33	-3.59	<b>1.74</b>

Pentacene derivatives **1**,  $\pm 2$ , and the mixture of  $\pm 3$  and  $\pm 4$  were subsequently subjected to identical photooxidation conditions ( $2 \times 10^{-4}$  M solutions in  $\text{CH}_2\text{Cl}_2$ , 25 °C, ambient light, exposed to air). Solution phase stabilities were studied by monitoring changes in UV-vis spectra as a function of time with direct exposure to light and air. Monosulfoxide  $\pm 2$  had a much longer half-life than **1** suggesting a highly favorable electronic effect. Derivative  $\pm 2$  was in fact the longest lived pentacene derivative known. Because it also showed exceptional solubility in a variety of organic solvents, it seemed a prime candidate for solution processed thin film electronic device study. Interestingly and unexpectedly, the half-life for the mixture of  $\pm 3$  and  $\pm 4$  was substantially reduced as compared to **1**. It is possible that the presence of two sulfoxide functions somehow sped the photooxidation according to an unknown mechanism, or that the mixture of  $\pm 3$  and  $\pm 4$  degraded in solution in a non-photooxidation manner. These possibilities warrant further study.



### 3.4 Control -Experimental: 6,13-diphenylpentacene with *m*CPBA

As a control experiment, 6,13-diphenylpentacene (**5**) was reacted with approximately two equivalents of *m*CPBA in dichloromethane. The crude reaction mixture was characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and mass spectrometry, revealing formation of 5,14-dihydroxy-5,14-dihydro-6,13-diphenylpentacene (**6**) as a single isomer. This was isolated in 19 % yield using preparative silica thin layer chromatography (Scheme 2) and was believed to form according to the mechanism proposed in Scheme 3. Thus, in the absence of sulfide functional groups, *m*CPBA reacted with the acene  $\pi$  system under the reaction conditions employed.



**Scheme 2.** Reaction of 6,13-diphenylpentacene **5** with *m*CPBA to form, 5,14-dihydroxy-5,14-dihydro-6,13-diphenylpentacene **6**

## CONCLUSION

Recent interest in the use of organic semiconductors has sparked widespread studies into the optimization of such devices for practical and efficient use and application of the devices in energy producing mechanisms. Organic semiconductors present much potential for industrial use because of their possible low cost of production. Pentacene and pentacene derivatives are revered as promising candidates for organic semiconductor research because they exhibit similar conduction mechanisms to inorganic semiconductors in addition to their organic semiconductor properties. The research was performed in order to prepare the chemoselective oxidation of a sulfide function on 6,13-*Bis*(decylthio)pentacene, **1**, using different equivalents of *m*CPBA. The reaction between **1** and approximately 0.5 equivalents of *m*CPBA was determined to be the best condition to produce an exceptionally long lived, monosulfoxide derivative,  $\pm$  **2**, that displayed excellent solubility. Chemoselective formation of monosulfoxide functions on either alkylthio or arylthio substituted acenes may prove to be an effective design strategy for the formation of robust species. The same cannot be said for the corresponding bissulfoxide derivatives. Reaction between **1** and approximately 2 equivalents of *m*CPBA led to  $\pm$  **3** and  $\pm$  **4**, a mixture of diastereomeric bissulfoxides that showed reduced photooxidative stability as compared to **1**.



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## APPENDIX

Figure 8.  $^1\text{H}$  NMR of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )

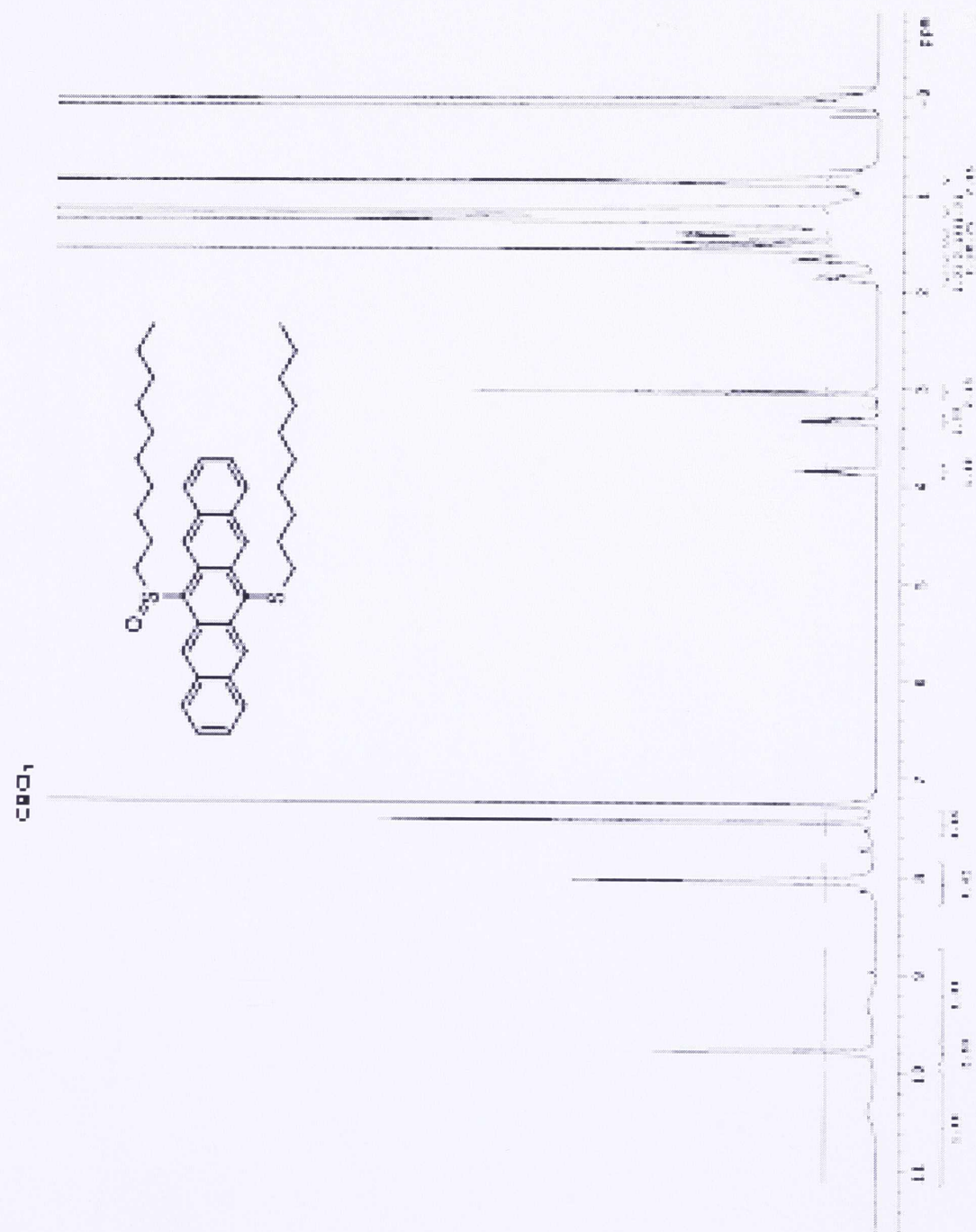




Figure 9.  $^1\text{H}$  NMR of 6-decylsulfanyl-13-decylthiophentacene ( $\pm 2$ )

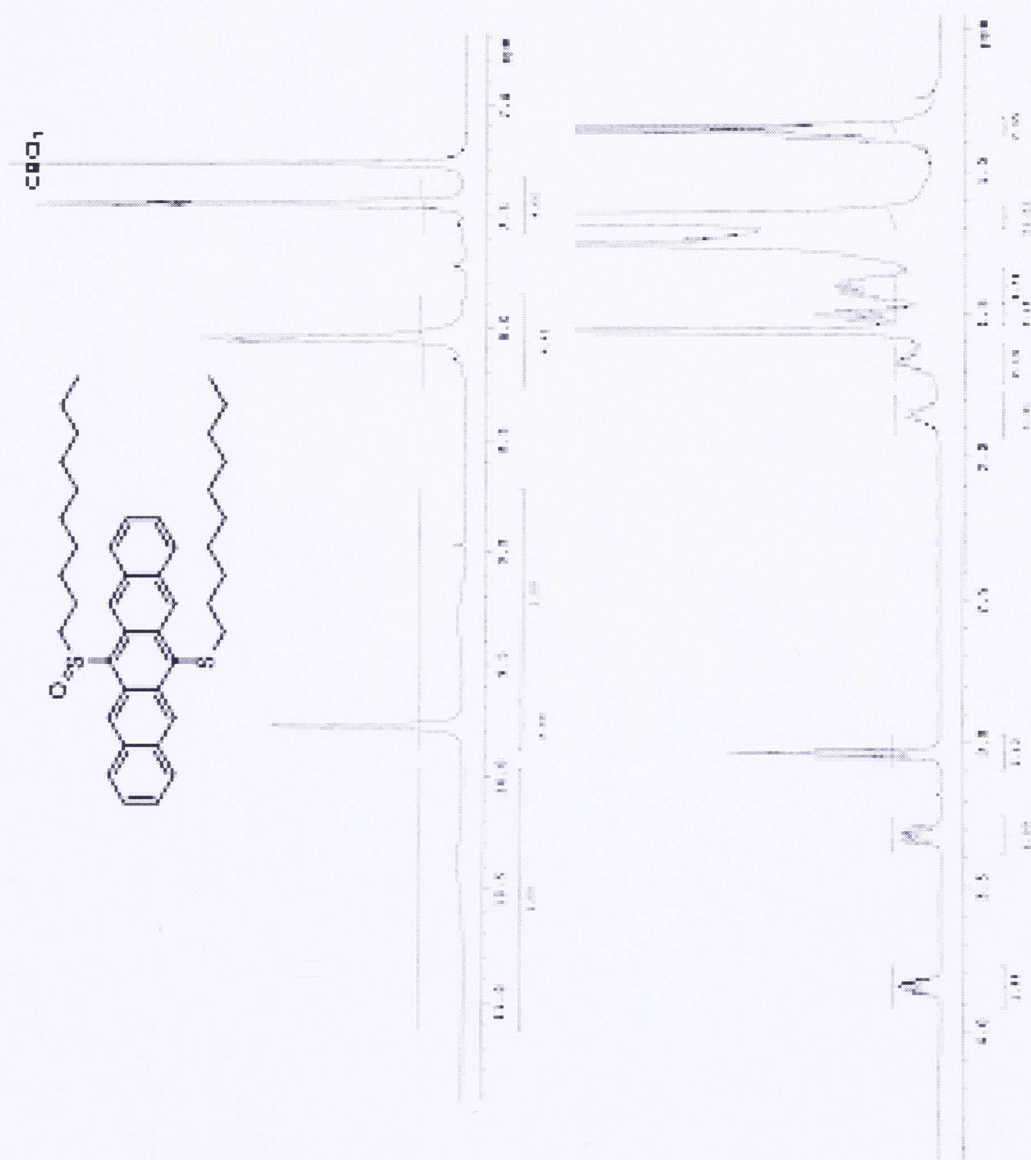


Figure 10.  $^{13}\text{C}$  NMR of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )





Figure 11. LDI-MS of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )

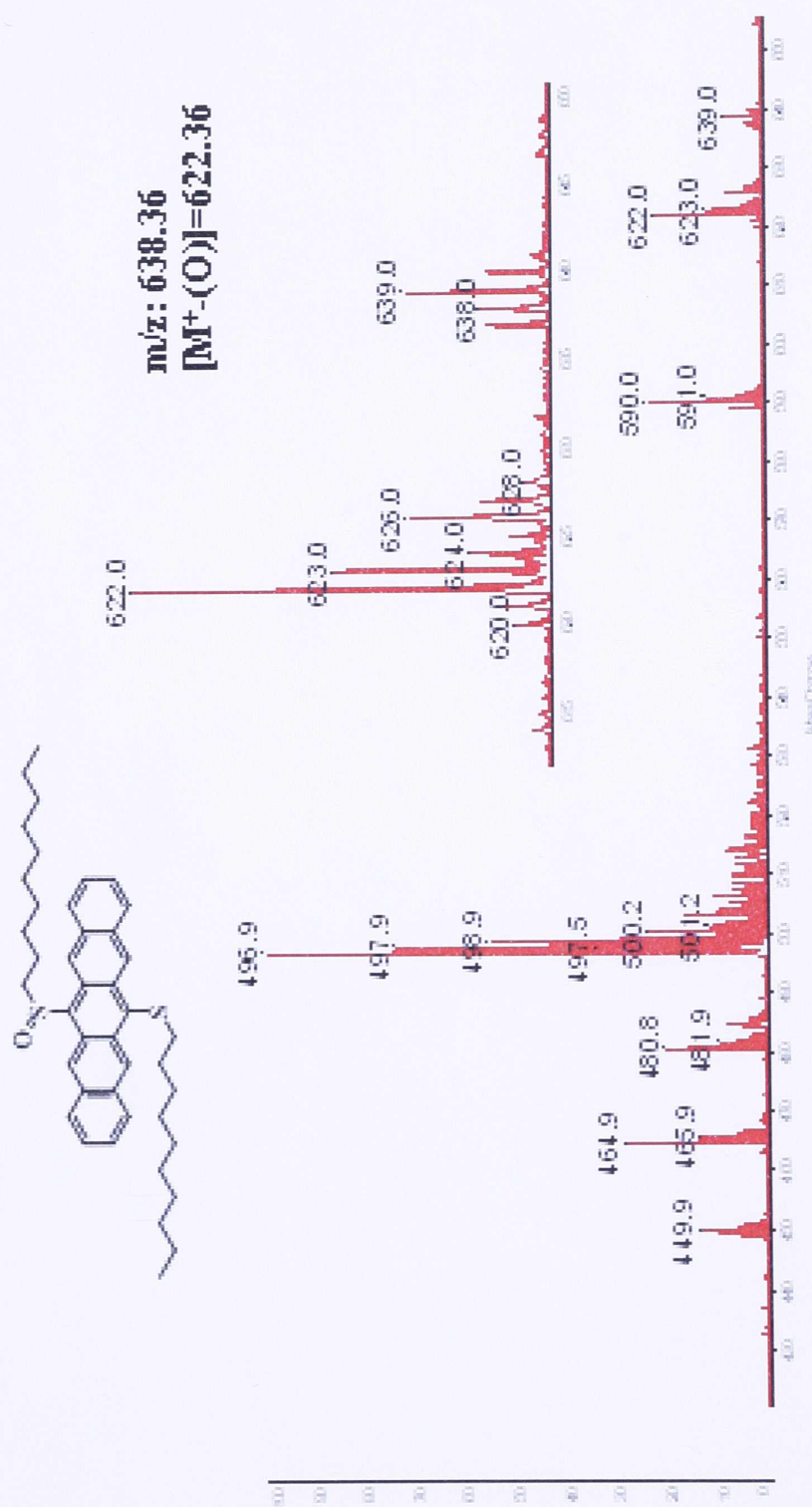


Figure 12.  $^1\text{H}$  6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )

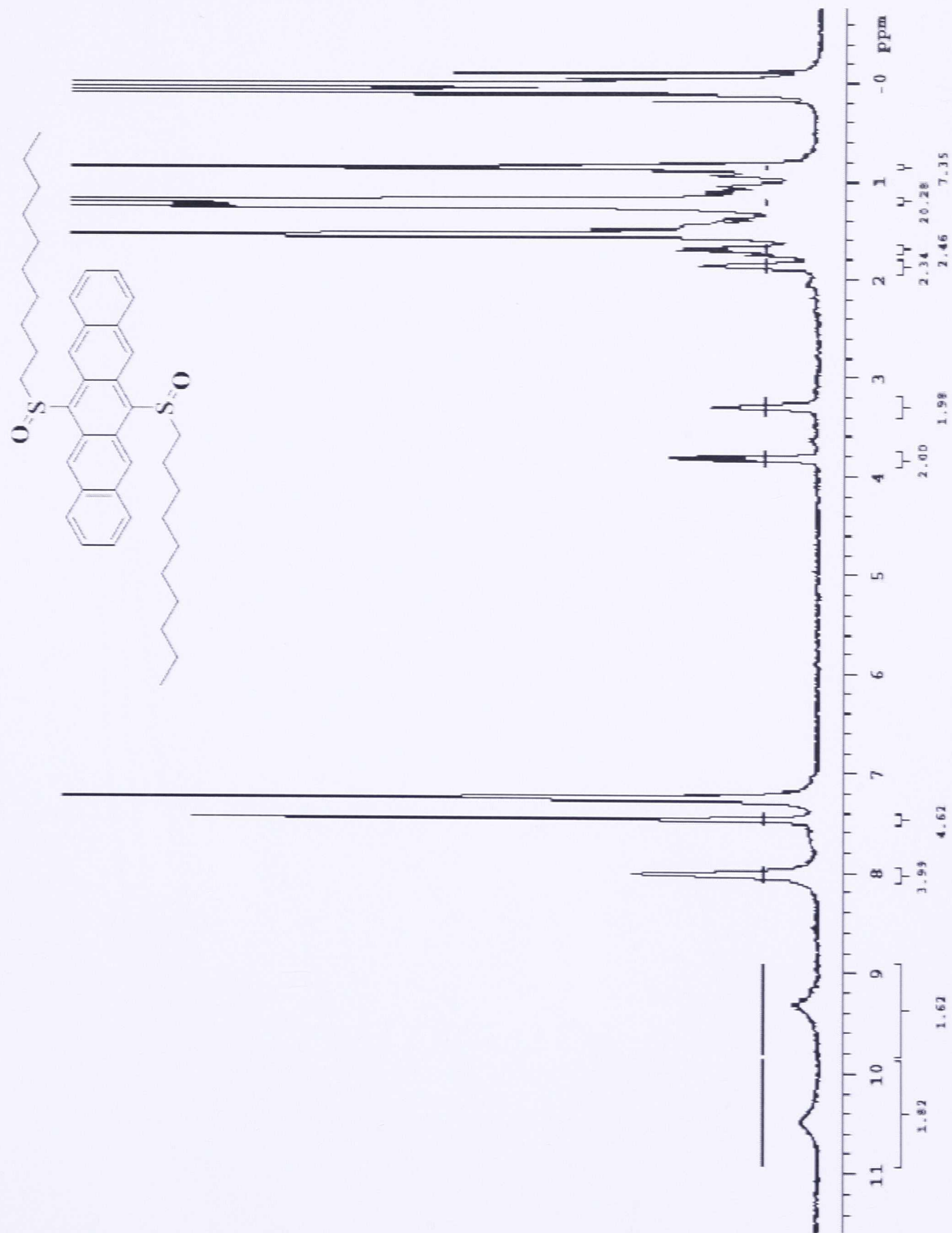




Figure 13.  $^1\text{H}$  6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )

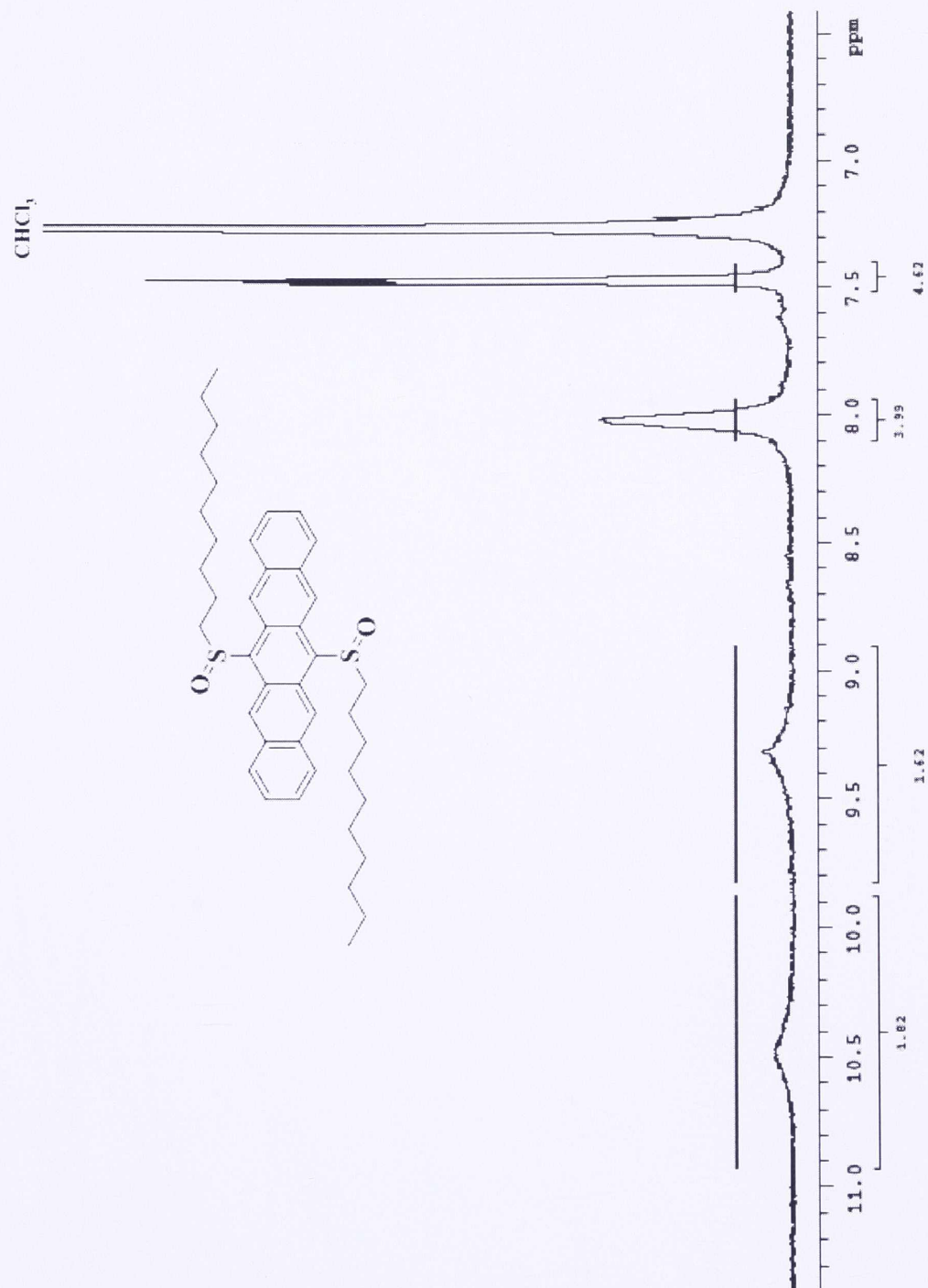
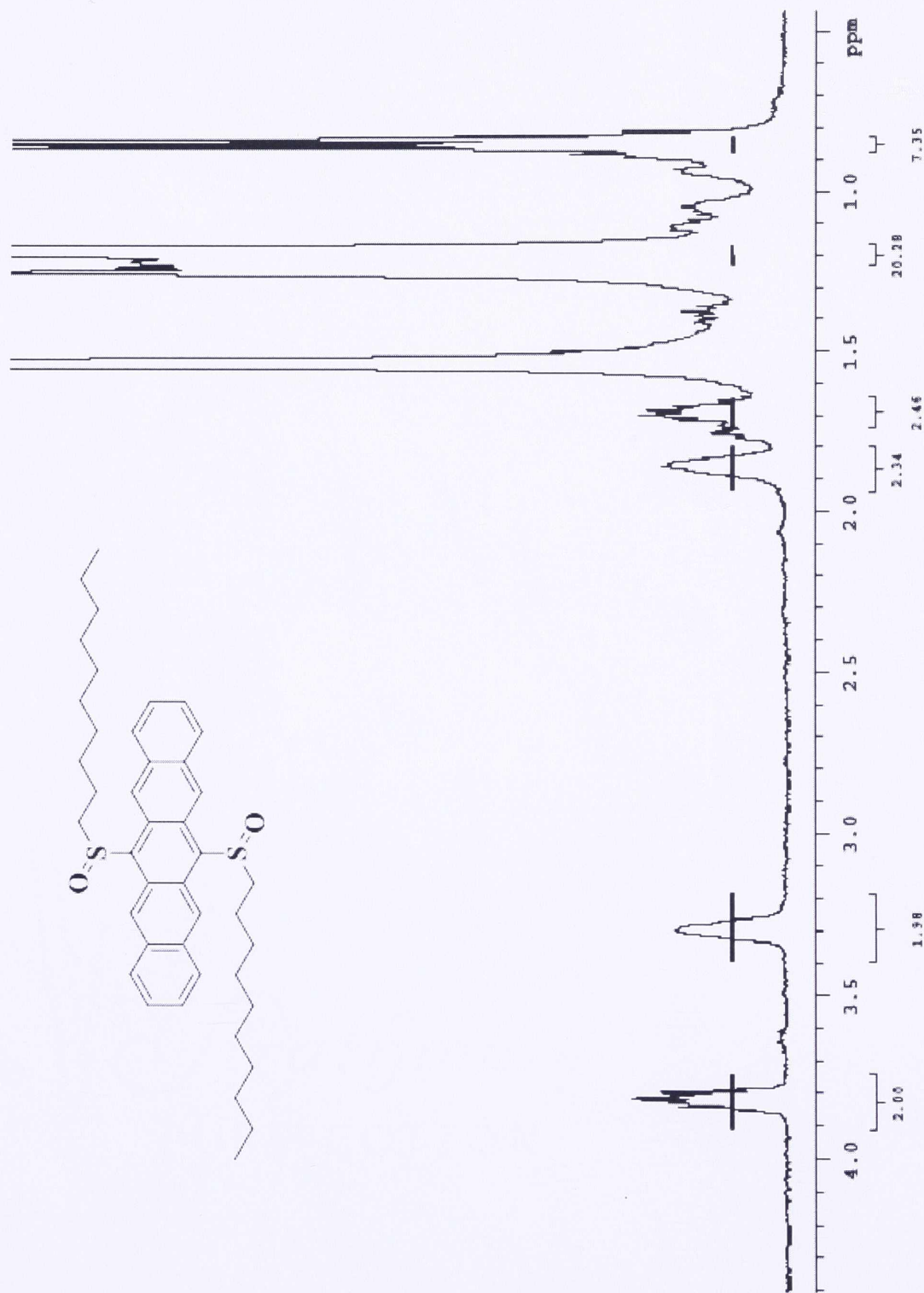


Figure 14.  $^1\text{H}$  6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )





**Figure 15. LDI-MS of 6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )**

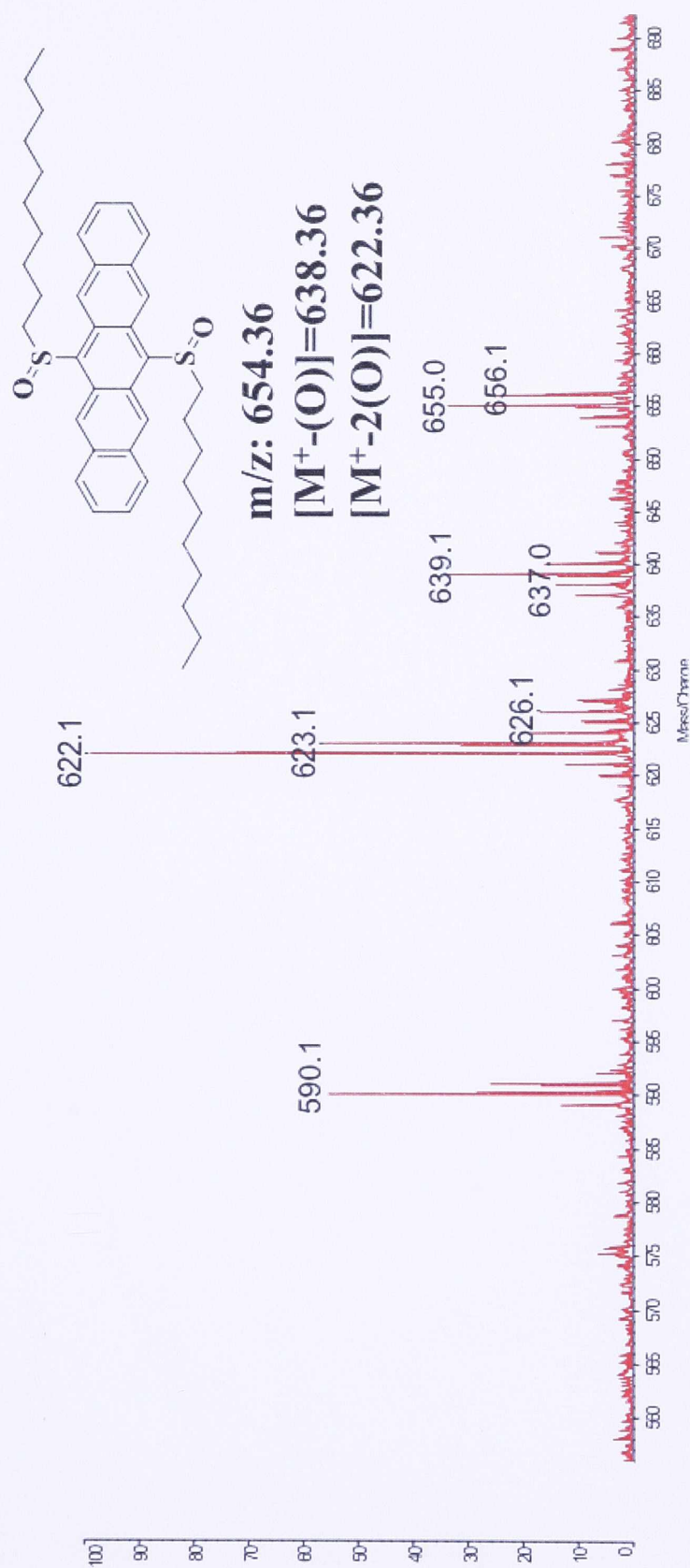


Figure 16.  $^1\text{H}$  NMR of 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol (6)

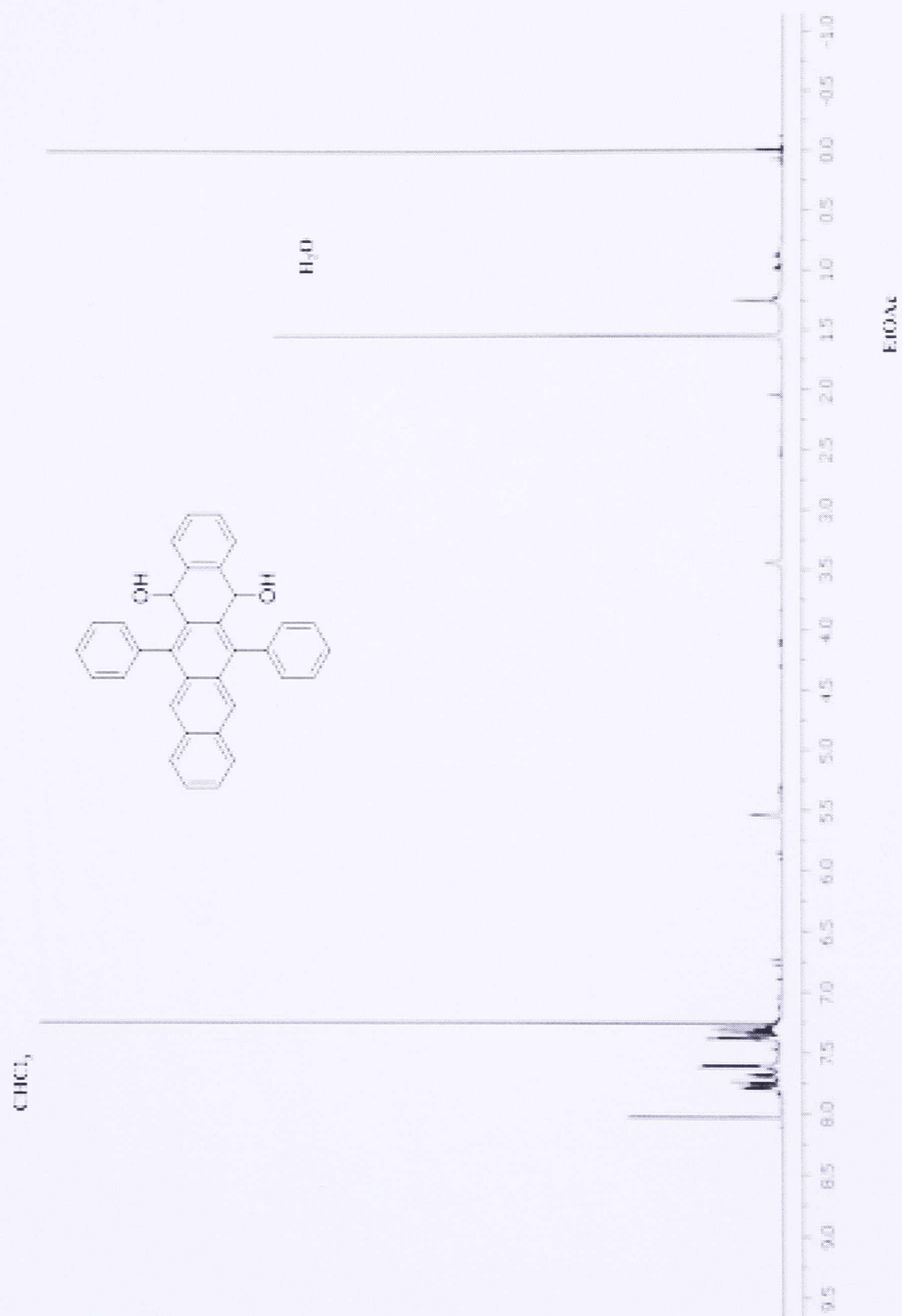




Figure 17.  $^1\text{H}$  NMR of 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol (6)

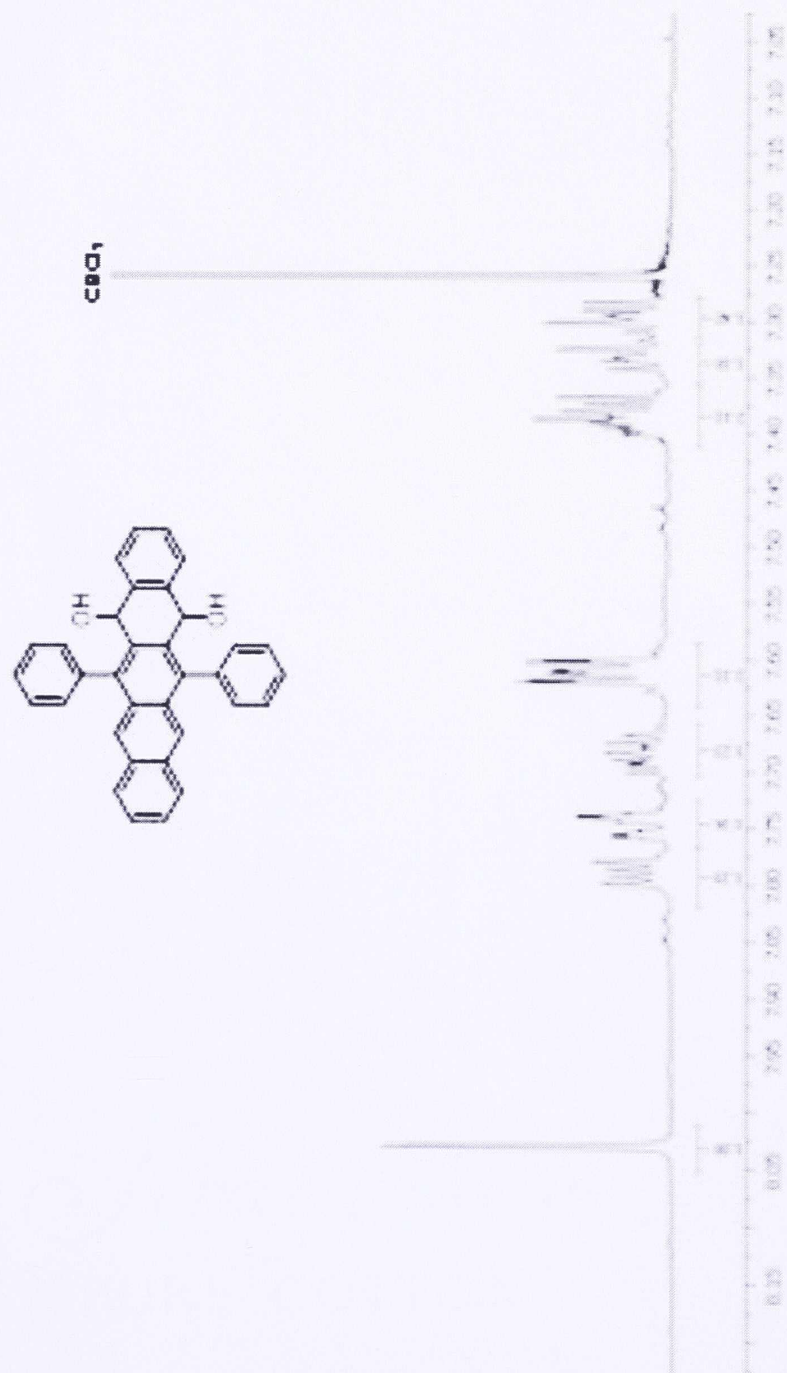


Figure 18.  $^{13}\text{C}$  NMR of 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol (6)

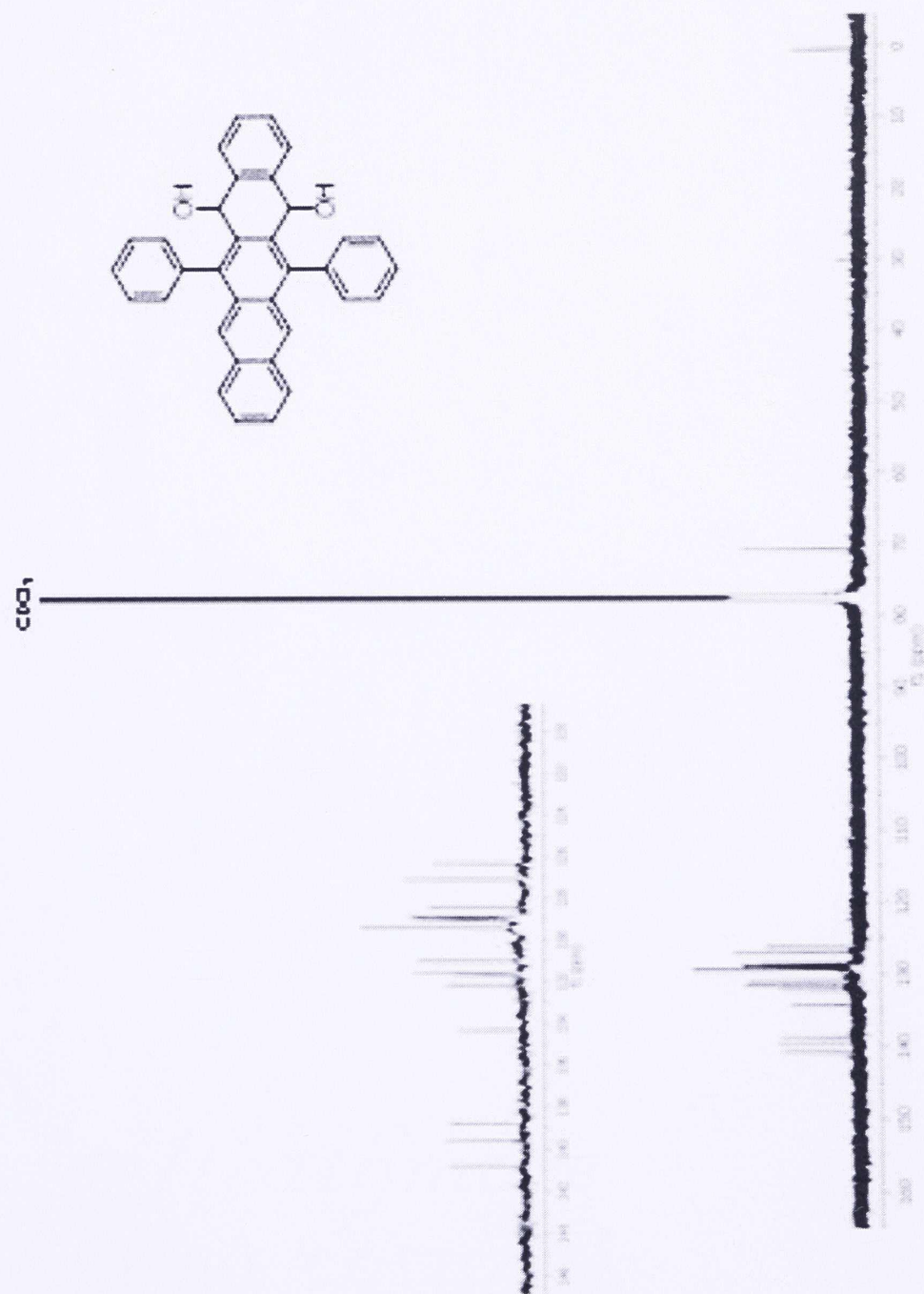
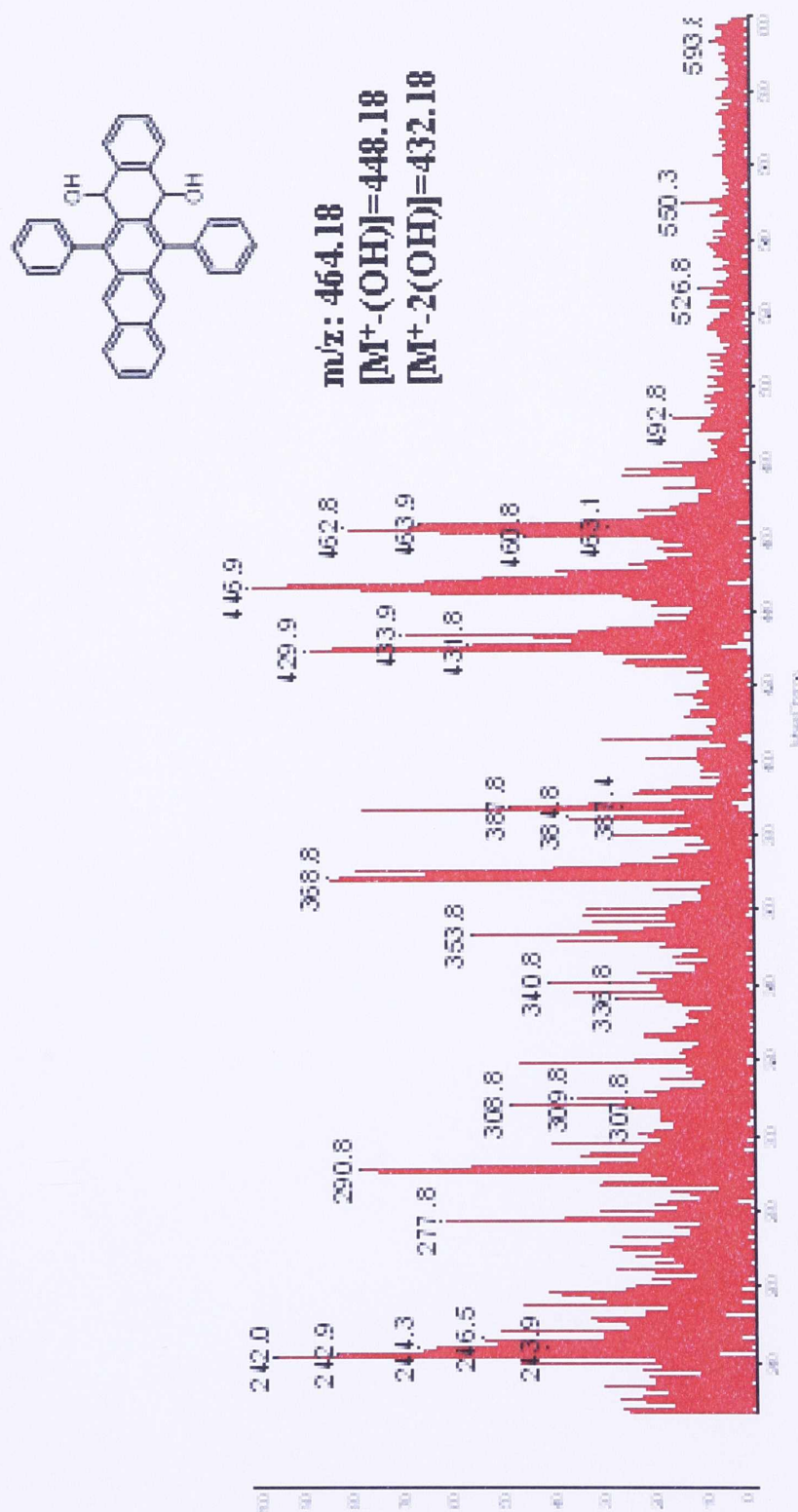
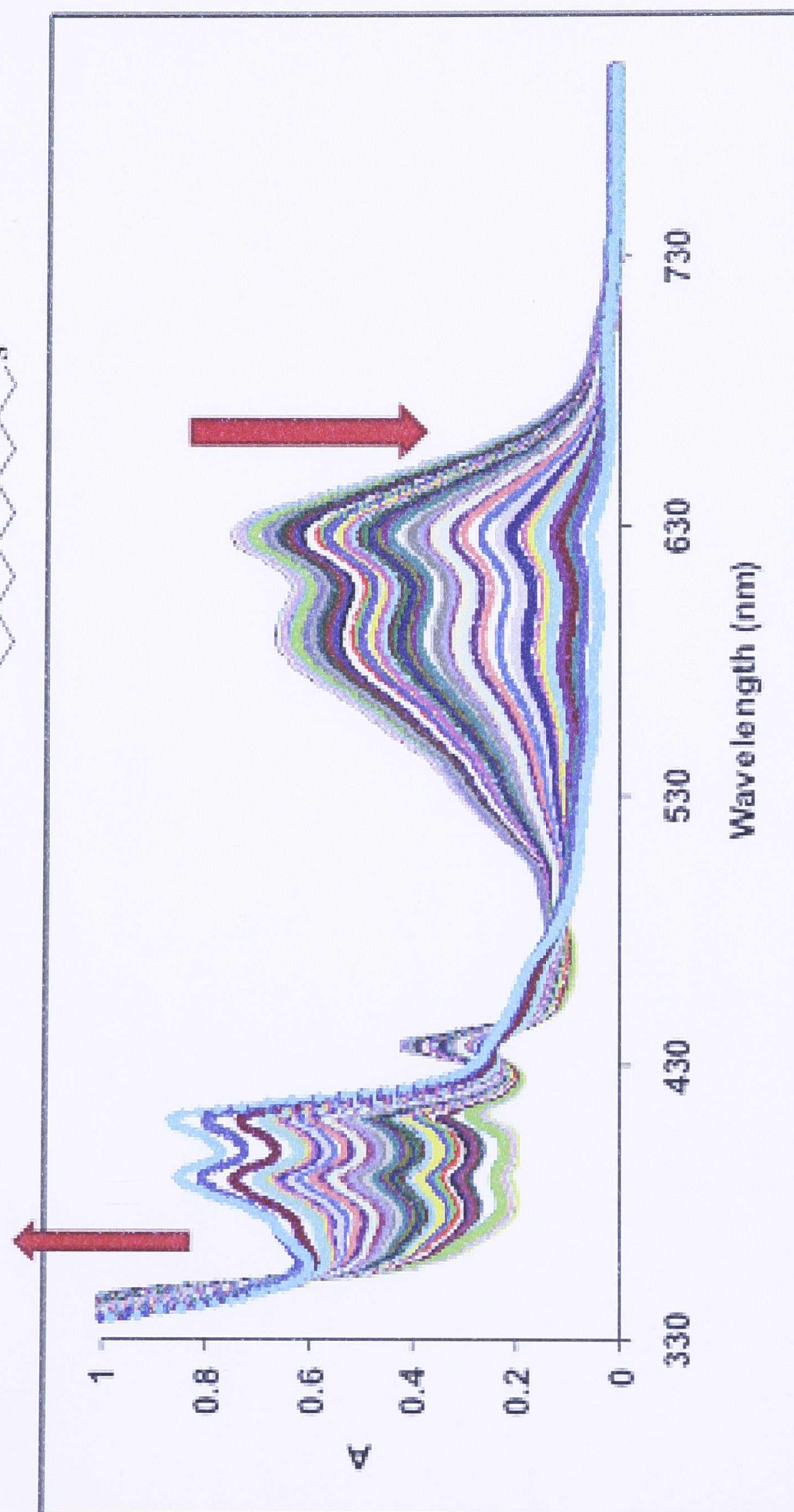
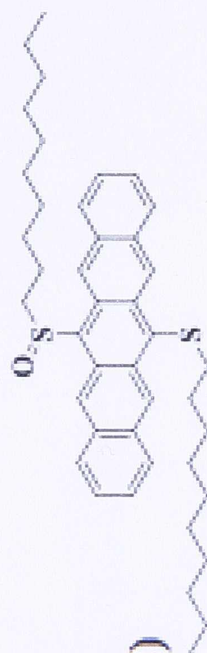




Figure 19. LDI-MS of 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol (6)



**Figure 20. UV-Vis spectra associated with the photooxidation of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )**





**Figure 21. UV-Vis spectra associated with the photooxidation of 6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )**

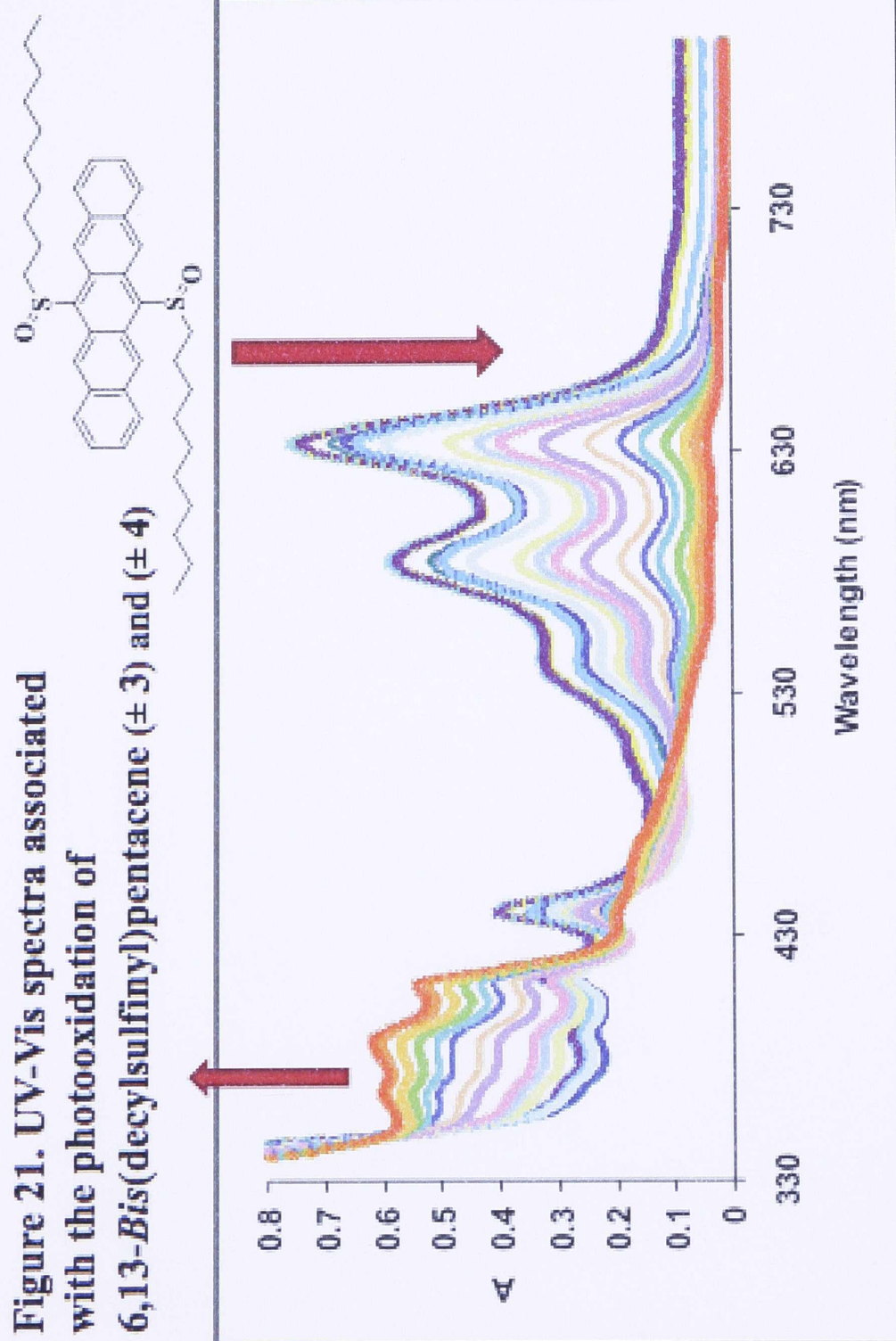


Figure 22. Comparison UV-Vis spectra of 6,13-Bis(decylthio)pentacene (1), 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ ), 6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )

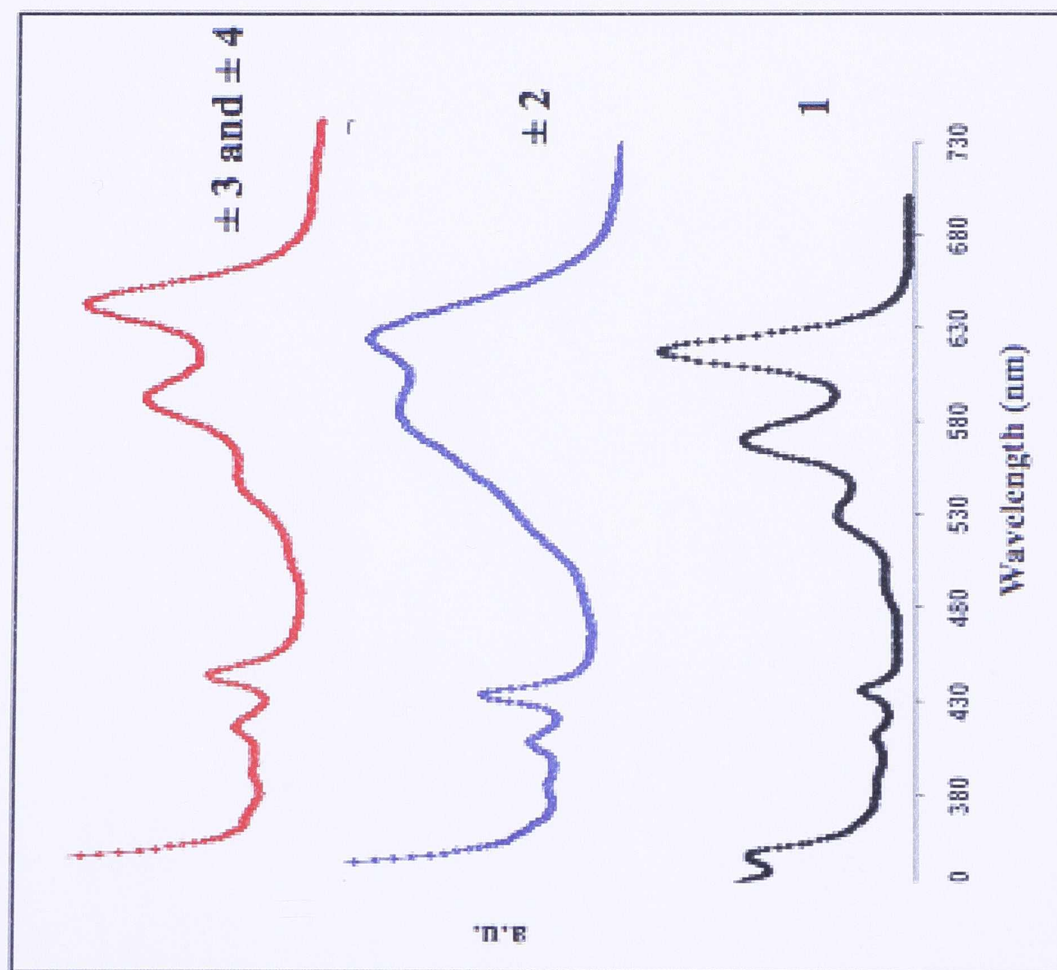
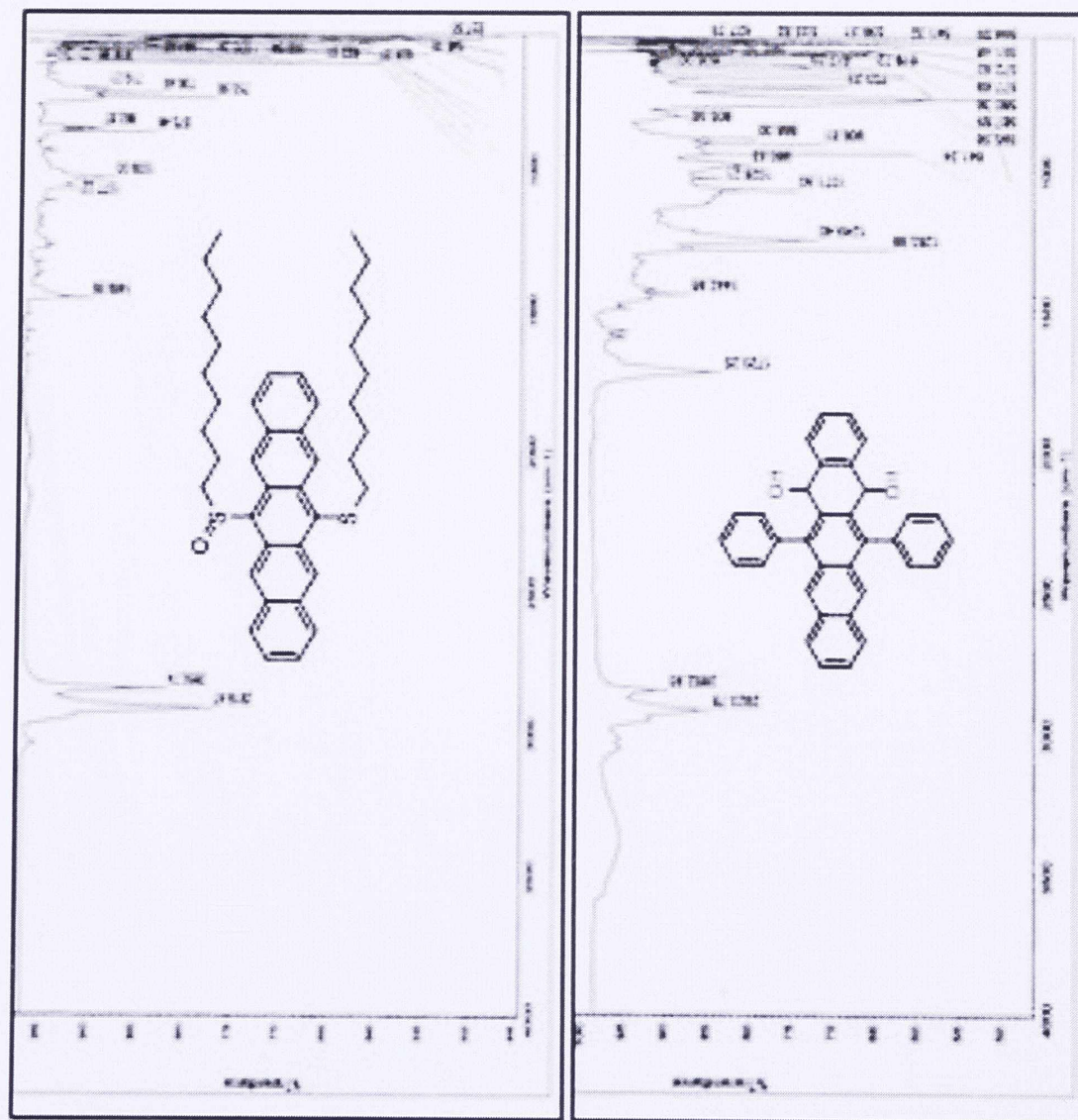




Figure 23. IR spectra of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ ) and 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol (6)



**Table 1. Spectral data of 6,13-pentacenequinone**

<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	δ 8.96 (s, 4H), 8.14 (m, 4H), 7.72 (m, 4H)
<sup>13</sup> C NMR (125.68 MHz, CDCl <sub>3</sub> )	δ 183.2, 135.47, 130.80, 130.30, 129.98, 129.66
LDI-MS <i>m/z</i>	308 [M <sup>+</sup> ]

**Table 2. Spectral data of 6,13-dihydroxy-6,13-dihydropentacene**

<sup>1</sup> H NMR (500 MHz, DMSO- <i>d</i> <sub>6</sub> )	δ 8.12 (s, 4H), 7.95 (m, 4H), 7.48 (m, 4H), 6.63 (s, 2H), 5.81 (s, 2H)
<sup>13</sup> C NMR (125.68 MHz, DMSO- <i>d</i> <sub>6</sub> )	δ 138.19, 131.67, 127.47, 125.44, 120.91, 66.98
LDI-MS <i>m/z</i>	312 [M <sup>+</sup> ], 295 [M <sup>+</sup> -OH], 278 [M <sup>+</sup> -2(OH)]

**Table 3. Spectral data of *cis*-6,13-Bis(*n*-decylthio)-6,13-dihydropentacene**

<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	δ 7.86 (m, 4H), 7.74 (s, 4H), 7.51 (m, 4H), 5.24 (s, 2H), 2.67 (t, 4H, <i>J</i> = 7.40 Hz), 1.69 (m, 4H), 1.42 (m, 4H), 1.30 (m, 24H), 0.93 (t, 6H, <i>J</i> = 6.63 Hz)
<sup>13</sup> C NMR (125.68 MHz, CDCl <sub>3</sub> )	δ 135.25, 132.60, 127.66, 127.40, 126.20, 47.99, 33.89, 32.04, 29.72, 29.69, 29.46, 29.43, 22.30, 29.26, 22.82, 14.26.

**Table 4. Spectral data of preparation of 6,13-Bis(*n*-decylthio)pentacene**

<sup>1</sup> H NMR (500 MHz, CDCl <sub>3</sub> )	δ 9.71 (s, 4H), 8.05 (m, 4H), 7.40 (m, 4H), 3.03 (t, 4H, <i>J</i> = 7.07 Hz), 1.55 (m, 4H), 1.41 (m, 4H), 1.25 (m, 4H), 1.16 (m, 20H), 0.86 (t, 6H, <i>J</i> = 7.07 Hz)
<sup>13</sup> C NMR (125.68 MHz, CDCl <sub>3</sub> )	δ 132.9, 132.84, 132.14, 128.90, 127.04, 125.98, 38.15, 31.99, 30.16, 29.65, 29.63, 29.39, 29.28, 29.01, 22.79, 14.24
UV-vis λ <sub>max</sub> (nm)	617, 570, 529



**Table 5. Spectral data of 6-decylsulfinyl-13-decylthiopentacene ( $\pm 2$ )**

$^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )	$\delta$ 10.40 (bs, 1H), 9.80 (s, 2H), 9.30 (bs, 1H), 8.10 (m, 4H), 7.50 (m, 4H), 3.90 (m, 1H), 3.35 (m, 1H), 3.18 (t, 2H), 1.90 (m, 2H), 1.70 (m, 2H), 1.60 (m, 2H), 1.50 (m, 2H), 1.2 (m, 24H), 0.90 (t, 6H)
$^{13}\text{C}$ NMR (100 MHz, $\text{CDCl}_3$ )	$\delta$ 138.22, 133.07, 132.84, 132.37, 130.72, 130.40, 130.09, 129.32, 128.04, 127.22, 126.85, 122.73, 54.49, 38.93, 32.41, 30.61, 30.06, 30.02, 29.90, 29.83, 29.80, 29.69, 29.40, 29.32, 24.82, 23.23, 14.69
LDI-MS $m/z$	638.36 $[\text{M}^+]$ , 622.36 $[\text{M}^+-(\text{O})]$
HRMS (FAB) $m/z$	638.3689, (calcd $m/z$ = 639.3686, Error = -0.4 ppm)
UV-vis $\lambda_{\text{max}}(\text{nm})$	627, 590, 536.

**Table 6. Spectral data of 6,13-Bis(decylsulfinyl)pentacene ( $\pm 3$ ) and ( $\pm 4$ )**

$^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )	$\delta$ 10.50 (bs, 2H), 9.40 (bs, 2H), 8.00 (m, 4H), 7.50 (m, 4H), 3.80 (m, 2H), 3.30 (m, 2H), 1.85 (m, 4H), 1.16 (m, 28H), 0.88 (t, 6H)
LDI-MS $m/z$	654.36 $[\text{M}^+]$ , 638.36 $[\text{M}^+-(\text{O})]$ , 622.36 $[\text{M}^+-2(\text{O})]$
HRMS (FAB) $m/z$	654.3638 (calcd $m/z$ = 654.3614, Error = -3.6 ppm)
UV-vis $\lambda_{\text{max}}(\text{nm})$	634, 584, 544.

**Table 8. Spectral data of 6,13-diphenyl-5,14-tetrahydropentacene-5,14-diol**

$^1\text{H}$ NMR (500 MHz, $\text{CDCl}_3$ )	$\delta$ 8.03 (s, 2H), 7.79 (m, 2H), 7.75 (m, 2H), 7.68 (m, 2H), 7.62 (m, 4H), 7.39 (m, 4H), 7.33 (m, 2H), 7.30 (m, 2H), 5.54 (d, 2H), 3.43 (d, 2H, $\text{D}_2\text{O}$ exchangeable)
$^{13}\text{C}$ NMR (125 MHz, $\text{CDCl}_3$ )	140.80, 139.58, 138.78, 134.33, 132.18, 131.67, 131.59, 130.99, 129.41, 129.05, 128.97, 128.87, 128.46, 127.09, 126.34, 70.76
LDI-MS $m/z$	464.18 $[\text{M}^+]$ , 448.18 $[\text{M}^+-(\text{OH})]$ , 432.18 $[\text{M}^+-2(\text{O})]$
HRMS (FAB) $m/z$	464.2006 (calculated $m/z$ = 467.2030, Error = -5.2 ppm)

